

EFFECT OF THE POROUS STRUCTURE OF CHAR ON THE RATE OF GASIFICATION

E. Hampartsoumian, M. Pourkashanian, D.T. Trangmar and A. Williams
Department of Fuel and Energy, Leeds University
Leeds, LS2 9JT

INTRODUCTION

A detailed understanding of the reactions kinetic of coal/char gasification is required for the successful design and construction of coal gasifiers. The reactor design criteria are largely dependent on the coal/char reactivity with reactant gases, such as carbon dioxide, steam and hydrogen. Extensive studies(1-3) have been carried out to determine this for different experimental conditions (eg. pressure, temperature or reactant gases concentration). However most of these studies have concentrated either on the variation of overall reaction rate and for different feedstocks or on establishing the fundamental mechanisms of the reaction(4).

The experimental and theoretical analysis of solid/gas reaction rate is further complicated by shrinkage, mass transfer and changing surface area and porosity of the solid during reaction. The influence of the progressive evolution of the solid pore structure on the overall reactivity depends on whether the reaction rate is controlled by external diffusion only, by chemical kinetics, or by a combination of these two limits. Because of the continuous changes in the pore structure, simultaneous reactivity and pore structure studies are needed to obtain a realistic solid/gas reaction rate. In addition, the estimation of the effective diffusivity of the porous solid can provide information on the evaluation and importance of the intra particle diffusion limitation and therefore the influence of mass transfer on the overall reaction rate can be obtained.

The major objective of this work is to utilize the effectiveness factor as a tool in the analysis of the kinetics of gasification of char with carbon dioxide using both an experimental and theoretical approach. This was accomplished by investigating the relationship between the effectiveness factor and the physical properties of coal/char (eg. porosity and density) during the gasification process. The overall reaction rates of two U.K coal derived chars were measured gravimetrically and the progressive changes in pore structure and the subsequent implications for the controlling mechanism investigated.

2. EXPERIMENTAL PROCEDURE

Two coals were sized to $<90 \mu\text{m}$ and pyrolysed by passing through a rich methane/air flame ($\phi = 0.72$). The coal particles were pyrolysed under rapid heating conditions ranging from 10^4 - 10^5 K/s and with temperatures approaching 2000 K. The char particles produced were collected after a total residence time of 180 - 200 ms. The proximate and ultimate analysis and the physical properties of the parent coals and chars used are shown in Table 1.

The N_2 and CO_2 surface areas of the samples were determined using a Quantisorb continuous flow analyser working with He/N_2 and He/CO_2 mixtures at 77 K. The percentage porosity of the samples were obtained from the measured apparent and

true densities of the chars. The values of true and apparent densities were obtained by He and Hg displacement techniques respectively.

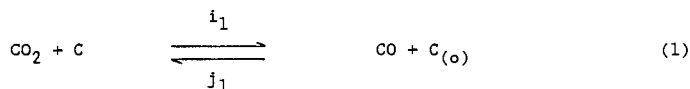
Gasification experiments with CO_2 as a reactant gas were conducted over the temperature range 1023-1273 K following the experimental procedures outlined previously(5). A thermogravimetric reactor system was used to monitor the changes in the char mass by recording the sample weight and reaction temperature. In each run, a reactant gas mixture comprising of CO_2/N_2 was passed into the reactor containing around 3 mg of char particles placed as a single layer held on a screen pan. The reactivity experiments consisted of initially heating the char to the target temperature at a rate of $50^\circ\text{C}/\text{min}$ in flowing nitrogen. The sample was then held at this temperature for 10 minutes and, after thermal equilibrium was established, the gas flow was switched to the reactant gases. In addition some reactant gas mixtures containing known concentrations of CO were also used in order to investigate CO inhibition of the char/carbon dioxide gasification reaction. The total gas flow rate was kept high enough so that the role of external mass transfer could be discounted as a possible rate limiting step.

Changes in physical properties of the char at different conversions were obtained by allowing the sample to react to target conversion and, at that point, replacing the flow of reactant gases by the nitrogen and allowing the reactor to cool to room temperature.

3. EXPERIMENTAL RESULTS AND DISCUSSION

(a) Reaction Kinetics:

The reaction of carbon with carbon dioxide can be expressed as:



where C_f and $\text{C}_{(o)}$ represent active site and a site possessing an oxygen atom. This reaction takes place at the surface of the carbon where carbon dioxide dissociates at an active site of the carbon surface releasing a molecule of carbon monoxide. This reaction is followed by the gasification of solid carbon to form a gas phase



The above chemical reactions are based on an oxygen exchange reaction mechanism. Previous studies(6-8) have shown that Langmuir-Hinshelwood theory can be used to treat the kinetics of C - CO_2 reaction. By applying a steady state assumption to $\text{C}_{(o)}$ and assuming that the number of free sites remain constant with burn off ($n = 1$), the overall rate of gasification can be shown as:

$$\text{Rate} = \frac{1}{w_o} \frac{dw}{dt} = \frac{k_1 P_{\text{CO}_2}}{1 + k_2 P_{\text{CO}} + k_3 P_{\text{CO}_2}} \quad (3)$$

where the k 's are generally a function of the rate constants for the elementary steps of reaction 1 and 2 and $k_1 = i_1$, $k_2 = j_1/j_2$ and $k_3 = i_1/j_2$. The initial

weight of the dry-ash free char is given by w_o and dw/dt is the average rate of weight loss. Equation 3 indicates that the presence of CO produced by the reactions 1 and 2 has the effect of retarding it (i.e. reaction j_1), therefore the retarding effect of CO was also investigated.

The equation 3 was solved by keeping the ratio of P_{CO}/P_{CO_2} constant and varying P_{CO_2} , i.e.

$$\frac{1}{R} = \frac{1}{k_1} \left[\frac{1}{P_{CO_2}} \right] + \left[\frac{k_2}{k_3} \right] \quad (4)$$

From a plot of $1/R$ vs $1/P_{CO_2}$ at a fixed temperature, values of k_1 and k_3 were obtained. The values of k_2 were evaluated by rearranging equation 3 and using the experimental data at varying CO - CO₂ concentrations. The calculated rate constants, k_1 , k_2 and k_3 were plotted against $1/T$ as shown in Fig.1 for five of the reaction temperatures investigated. The experimental results indicate that the rate of oxygen exchange and carbon gasification increases with temperature in accordance with the change in their rate constant. Values for the activation energies (E) and pre-exponential factors (A) for the rate coefficient ratios are listed in Table 2. The equilibrium constant (K_{eq}) for the reaction (1) can be calculated from values of i and j , which is obtained from experimentally determined values of k_1 , k_2 and k_3 (7). The value of ΔH for reaction (1) obtained from thermochemical calculation is of order of 104 kJ. On the basis of an oxygen exchange mechanism, the heat of reaction for the first step of C - CO₂ reaction (i.e. reaction 1), was found to be 109 kJ/mole for char A and 120 kJ/mole for char B (endothermic). These values are larger than the calculated values, therefore indicating that the carbon oxygen bonded surface complex is an intermediate between single and double π bond but closer to that of double π bond.

From the values of activation energies (E_1 , E_j) it can be concluded that the reaction leading to the presence of oxygen atom from CO₂ on the carbon surface requires more energy than its removal by CO.

In theory the values of k_2 and k_3 , which are the intrinsic reaction rate ratios, should be independent of the char type at a given temperature. Similarly the values of E_{j1} , E_{j1} and E_{j2} should be independent of the type of char used. However, it is noted that the values of E_{j1} , E_{j1} and E_{j2} determined from equation 3 are influenced by the char type. This variation in the activation energies can be related to few factors such as (i) the presence of the inorganic impurities in the char which will influence the reaction rate by acting as a catalyst and (ii) the variation in the pore growth and coalescence during the gasification process which will influence the intraparticle diffusional limitations.

(b) Effects of pore diffusion:

The overall rate of reaction on a porous char depends upon the extent of the internal surface and the size of the pores comprising this surface. In addition the pore structure of the char particles change during the gasification process. The quantitative analysis of the problem of pore diffusion of reactant gases coupled with the pore surface reaction was carried out by Thiele(9), where he introduced the concept of effectiveness factor (η). The effectiveness factor is a useful indicator of the amount of limitation due to boundary layer and in pore

diffusion. The effectiveness factor at any instant during the reaction is defined as

$$\eta = \frac{\text{overall reaction rate of particle}}{\text{reaction rate when reactant concentration throughout the particle were equal to that in free stream.}} \quad (5)$$

Solving equation 5 for spherical geometries which is modified to include overall fractional solid conversion term (x) gives:

$$\eta = (1-X) \left[\frac{3}{\phi_m} \right] \left[\frac{1}{\tanh \phi_m} - \frac{1}{\phi_m} \right] \quad (6)$$

where ϕ_m is the modified Thiele modulus. From the experimental results the initial modified Thiele modulus was calculated and the contribution of pore diffusion effect during the gasification process obtained. In order to investigate the influence of the pore diffusion, the observed fractional rate (dx/dt) for char B was plotted against 1/T at 30% carbon conversion as shown in Fig. 2. The results indicate that for the temperature range 1023-1173 K the plot is reasonably linear over the experimental points but at higher temperature the experimental values are below the line. The intraparticle diffusional limitation effect over the chemical reaction rate can be determined by calculation of the intrinsic chemical reaction rate [(dx/dt)/ η] using the calculated effectiveness factor. Fig. 3 shows the plot of intrinsic chemical reaction rate against 1/T for the char B. Results indicate that all experimental points are on the straight line and therefore the effectiveness factor is used as a correction factor to eliminate the effect of the intraparticle diffusion at a region where the reaction rate is controlled by both chemical and mass diffusion.

The effectiveness factor at different carbon conversions can be predicted(10) from the values of relative physical and structural properties of char using the equation below:

$$\eta = (1-X)^{n/2} a^{-X/2} \left[\frac{(\rho_T^X / \rho_T^0) D_e}{(\rho_a^X / \rho_a^0) \theta^X / \theta^0} \right]^{0.5} \quad (7)$$

where ρ_a^0 , ρ_T^0 , ρ_a^X , ρ_T^X and θ are the initial apparent and true densities and apparent and true densities at different carbon conversion and porosity of char respectively. Note that n is proportional to the number of active sites and a is a constant related to the ratio of adsorption constant and an effective diffusivity of CO_2 (D_e). The predicted effectiveness factor was based on isothermal reaction with no fluid film diffusion resistance.

The predicted η values for char A were first plotted against carbon conversion as shown in Fig. 4. and then compared with the calculated values and the influence of a and n investigated. The limiting case (i.e. $a = 1$ and $n = 1$), assuming that all the active sites remain available for gasification process, are also shown in Fig. 4 as well as the the variation of porosity with carbon conversion. The best prediction of η was obtained when $a = 1$ and $n = 1.5$.

CONCLUSIONS

From the rate of reaction between porous chars and carbon dioxide, it can be concluded that two stage oxygen exchange mechanism holds. The L - H type rate expression are capable of representing the data in a temperature range of 1023 - 1223 K.

The effect of mass transfer on the rate of carbon-carbon dioxide reaction occurring in a porous char was analysed. Results indicate that intraparticle diffusional limitation becomes significant at $T \geq 1173$ K. The estimated effectiveness factor based on the variation of physical properties of char during the gasification process can be used to investigate the influence of the pore diffusion limiting of reactant gases at different experimental conditions.

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Table 1: Proximate, ultimate and physical properties of parent coals and produced chars.

	Coal A Markham-Main NCB Rank 702	Coal B Linby NCB Rank 800	Char A	Char B
Proximate Analysis (%)				
Moisture	5.88	8.4	2.67	4.02
Volatile matter	34.09	31.0	5.36	5.70
Ash	2.47	9.4	8.95	18.97
Fixed carbon	57.56	51.2	83.02	71.31
Ultimate Analysis (%)				
Carbon	81.12	79.80	89.38	89.14
Hydrogen	4.48	5.40	0.96	0.74
Nitrogen	1.67	1.61	1.62	1.85
Physical Properties				
True density (g/cm ³)	1.35	1.28	1.511	1.382
N ₂ surface area (m ² /g)	11.94	14.07	34.56	28.13
Porosity %	18.50	16.80	57.	51.

Table 2: Arrhenius constants for the C - CO₂ reaction.

k = A exp(-E/RT) E = kJ/mole	Char A	Char B
k ₁ (g g ⁻¹ s ⁻¹ atm ⁻¹)	4.26 x 10 ⁴ exp(-187.1/RT)	8.32 x 10 ⁴ exp(-177.7/RT)
k ₂ (atm ⁻¹)	7.24 x 10 ⁻⁶ exp(138.2/RT)	2.91 x 10 ⁻⁶ exp(150.2/RT)
k ₃ (atm ⁻¹)	6.45 x 10 ⁻² exp(28.4/RT)	8.39 x 10 ⁻² exp(30.1/RT)
A _i (g g ⁻¹ s ⁻¹ atm ⁻¹)	4.26 x 10 ⁴	8.32 x 10 ⁴
E _i (kJ mole)	187.1	177.7
A _{j1} (g g ⁻¹ s ⁻¹ atm ⁻¹)	4.78	2.88
E _{j1} (kJ mole ⁻¹)	77.3	57.6
A _{j2} (g g ⁻¹ s ⁻¹)	6.45 x 10 ⁵	9.91 x 10 ⁵
E _{j2} (kJ mole ⁻¹)	216.4	207.8
K _{eq}	8.91 x 10 ³ exp(-109.8/RT)	2.89 x 10 ⁴ exp(-120.1/RT)
ΔH (kJ mole ⁻¹)	109.8	120.1

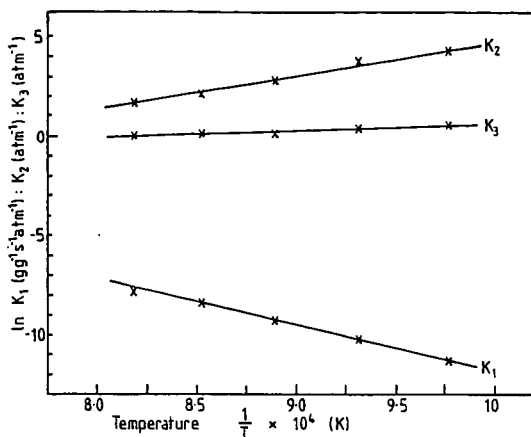


Fig. 1 Arrhenius plot of L-H equation constants for char A.

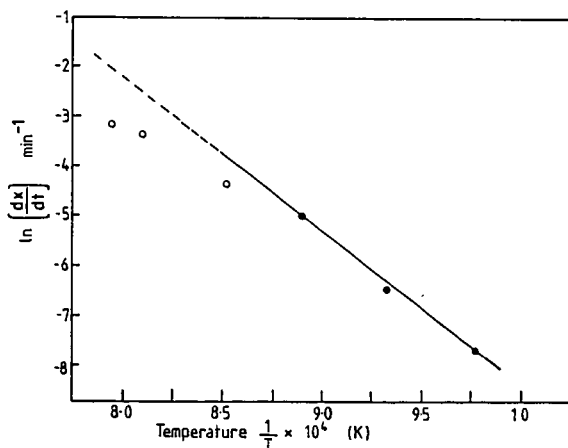


Fig. 2 Variation of observed reaction rate with temperature for char B at $X = 0.3$.
 ● chemical reaction control, O intra-particle diffusion effect on overall rate.

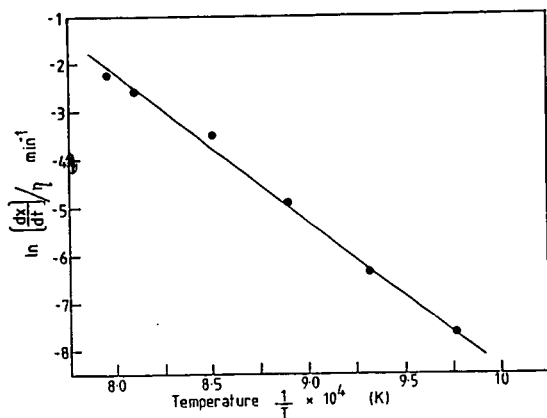


Fig.3 Variation of intrinsic chemical reaction rate with temperature for char B at $X = 0.3$.

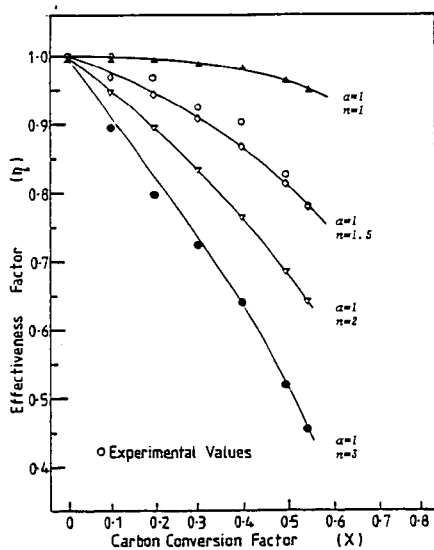


Fig.4 Comparison of predicted and experimentally obtained values of effectiveness factor for char A.